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TOXICS USE

THE MASSACHUSETTS TOXICS USE REDUCTION INSTITUTE

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Toxics Use Reduction

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What is Toxics Use Reduction?

Toxics Use Reduction (TUR) is a new environmental protection program that has been established in Massachusetts to promote safer and cleaner production that enhances the economic viability of Massachusetts firms. TUR is a fundamental form of pollution prevention that focuses on industrial activities.

The goal of the TUR program is to reduce the generation of hazardous wastes in Massachusetts by 50 percent by 1997 without limiting the capacity of local firms to grow and prosper. This is a statewide goal. Individual firms may set their own TUR targets.

The program was established in 1989 when the Massachusetts legislature unanimously passed the Toxics Use Reduction Act (TURA). This law was the result of a long negotiation between business and environmental interests that resulted in a bill endorsed by both.

How do firms implement Toxics Use Reduction programs?

The TUR program promotes several TUR techniques to reduce industrial waste streams. These include:

- toxic chemical substitution
- production process modification
- finished product reformulation
- production modernization
- improvements in operations and maintenance
- in-process recycling of production materials

Firms are encouraged to establish planning teams and engage the workforce in analyzing production processes, conducting materials accounting programs, auditing health and environmental regulations, and identifying TUR options. Potential options often require thorough financial and technical analyses to assess adoption feasibility. Upper level management commitment is often key to successful implementation of TUR programs.

Who is covered under TURA?

Not all Massachusetts firms are covered under TURA. First, a firm must be in an industry that falls within certain Standard Industrial Classification (SIC) codes. Second, a firm must have 10 or more employees. Third, a firm must use at least one of the chemicals on a specified state list in amounts that exceed established thresholds.

• Which industries are covered?

They include those in SIC codes 10-14 (mining), 20-39 (manufacturing), 40 and 44-49 (transportation), 50 and 51 (wholesale), and 72, 73, 75, and 76 (certain services).

• Which chemicals are covered?

Initially, all of the chemicals that are covered on the federal Toxics Release Inventory (under Section 313 of the federal Emergency Planning and Community Right to Know Act). This includes more than 300 toxic chemicals. The list increases over a three-year period to include by 1994 all of those chemicals covered under the federal Comprehensive Environmental Response and Compensation Liability Act (the "Superfund Law").

• What are the use thresholds?

A firm must manufacture or process 25,000 pounds per year of a listed chemical, or must use 10,000 pounds per year of a listed chemical.

How does a firm comply with TURA?

A firm covered under TURA must meet several requirements. These include filing an annual report, paying an annual fee, and, after 1994, preparing a TUR plan every other year.

• What are annual reports?

Each covered firm must file an annual report (called a "Form S"), which identifies the listed chemicals that the firm used during the year in each production process (called a "production unit"), the percentage reduction of toxic by-products and toxic emissions, and the TUR techniques used to reduce the wastes.

The percentage reductions are based on a base year that has been established by the firm (for most firms this is 1987, 1988, or 1989). There are two indices of reduction performance for each listed chemical. The "by-product reduction index" describes the percentage of nonproduct chemicals

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reduced per unit of product compared to the base year. The "emission reduction index" describes the percentage reduction of chemicals released from the plant per unit of product compared to the base year.

The TUR techniques employed to achieve these reductions are identified on a matrix supplied on the Form S.

- **How much is the fee?**

The fee was set to provide revenue for the state to administer the TURA program. Monies raised through the fee are set aside in a special trust fund which can be used only for the TURA program. The actual fees vary according to the size of the firm and the number of listed chemicals used above the annual threshold.

- **What is a toxics use reduction plan?**

After 1994 each firm must prepare a plan documenting how they will use TUR techniques to reduce the generation of wastes. Each plan must provide a corporate policy statement and two- and five-year goals for by-product reduction of each listed chemical. In addition, each plan must include information about current and projected toxic chemical use, the technical feasibility of implementing various techniques, and the economic impacts of each technique; a description of each technique or procedure that is to be implemented; and a schedule for implementation.

Each plan must be certified by a state-authorized Toxics Use Reduction Planner. A planner may be either an accredited employee of the firm or a licensed consultant trained by the Toxics Use Reduction Institute and certified by the Department of Environmental Protection.

What is Massachusetts government doing to promote TURA?

The Commonwealth is required to promote the state law through four institutions: the Administrative Coordinating Council, the Bureau of Waste Prevention, the Office of Technical Assistance, and the Toxics Use Reduction Institute.

The Administrative Coordinating Council brings together representatives from seven state agencies that oversee environmental, health, labor, and development programs. The purpose of the council is to establish more coordinated approaches promoting industrial development that is environmentally sound and enhances human health. The Council is assisted by an Advisory Committee made up of members of the public and the business community.

The Bureau of Waste Prevention is a reorganized unit within the state Department of Environmental Protection and

is charged with writing regulations, enforcing the law, and collecting and making data available.

The Office of Technical Assistance in the Executive Office of Environmental Affairs provides free technical consultation and assistance to firms attempting to implement TUR programs.

The Toxics Use Reduction Institute at the University of Massachusetts Lowell provides education and training in TUR for professionals and the general public, conducts a technology transfer program, and sponsors research in the development of safer materials and cleaner technologies.





Design for the Environment

What is Design for the Environment?

Design for the Environment (DfE) is an engineering design initiative that promotes environmentally sound decisions at every step of the production process from chemical design, process engineering, procurement practices, and end product specification to post-use disposal. The concept is developing in the environmental/engineering fields and is beginning to gain public recognition.

Where did the concept come from?

The idea emerged among environmental professionals in the American Electronics Association (AEA) during the late 1980s. DfE follows the popular engineering concepts of "concurrent engineering," "design for manufacturing," and "design for disassembly." AT&T has been a strong promoter of the concept. The U.S. Environmental Protection Agency (EPA) began an internal dialogue on the idea of DfE in 1991. Parallel concepts in Europe appear to have predated the AEA work, particularly in the areas of package design and industrial design.

Why consider DfE?

During the last six years, growth of interest and initiatives around the concept of pollution prevention and toxics use reduction has been significant. Firms around the world are beginning to recognize that it is far more efficient to prevent the generation of industrial wastes than to manage the wastes once they are produced. In the U.S., environmental engineers increasingly are engaging production engineers around reduction of waste streams from manufacturing processes. Yet this is only one avenue for bringing about environmentally sound production processes. The opportunity to consider environmental effects at the earliest design points in the development of new products or the redesign of current production processes opens up an exciting new area of professional work.

DfE's holistic approach is part of the broader concept of industrial ecology, first introduced to the general public in 1989 by Robert Frosch and Nicholas Gallopoulos, research scientists at General Motors. The industrial ecology view promotes sustainable manufacturing through the modeling of industrial processes after the material and energy flows of

the natural environment. An industrial ecosystem follows a cyclical model in which the consumption of energy and materials is optimized, waste generation is minimized, and the byproducts of one process become raw material for another.

DfE pursues industrial ecology principles by requiring that industrial designers and managers think in terms of cycles or complex systems rather than traditional linear process flow diagrams. DfE locates environmental concern within the most positive stages of the production process.

Rather than trying to mitigate environmental consequences of production after the products have been defined and the processes designed, DfE encourages consideration of environmental issues to help shape the context of

the industrial designer or process engineer in the same way that manufacturability, cost competitiveness, and consumer satisfaction currently shape that context.

Components of DfE

- product design
- packaging design
- product life-cycle analysis
- process engineering
- product design specifications
- engineering design education

How can DfE be promoted?

Industry is beginning to consider the environmental impact of a product throughout its life cycle, primarily because of regulatory trends and rising treatment and disposal costs. Corporations are also recognizing the potential economic advantage of DfE. But more training, technical information, and industry-specific knowledge of DfE are needed to bring about its broad-scale implementation.

Efforts to develop and integrate DfE into the production of products and services are under way in the public and private sectors. EPA's Design for the Environment Program, operating from the Office of Pollution Prevention and Toxics, is engaged in voluntary collaborative projects with industry, education, and the public at two levels:

Cooperative Industry Projects foster the development and use of DfE tools and principles in specific industries through the evaluation of alternative materials and processes in terms of their comparative risks, performance, and costs. Current

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projects involve the printing, dry cleaning, and computer and electronics industries. EPA seeks to establish projects with other industry segments as well.

Infrastructure Projects take a long term approach aimed at changing aspects of general business practices and developing incentives for environmental design. Work is under way with insurance and accounting professionals to incorporate pollution prevention considerations into analytic accounting and insurance risk management and underwriting systems. A grant program with universities and the National Science Foundation funds research into alternative approaches for the design and manufacture of chemicals. EPA also funds the development of university and college curricula that apply DfE principles in courses in business, engineering, and natural resources.

Several industries, particularly automotive and computer and electronics manufacturing, have initiated DfE efforts. A major thrust of these efforts is the design of products that can be recovered from end users and disassembled for recycling, remanufacture, or reuse. Other efforts include the American Electronics Association's DfE task force which produces a series of white papers on aspects of DfE; the American Institute of Architects' DfE programs for architects; and a major industrial initiative called the Design for Disassembly, Service and Environment Consortium. U.S. and Canadian industries and government agencies are participating in development of a North American Guideline for Environmental Design that will assist industrial designers and executives in meeting DfE principles.

How can DfE promote Toxics Use Reduction?

While TUR focuses on reducing the use or waste of toxic substances within existing industrial processes, DfE moves the focus of this effort to an earlier phase of the product life cycle. DfE considers environmental factors while products and processes are still on the drawing board. Essentially, TUR would be pre-built into industrial products and processes that were designed for the environment.

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Cleaner Production

What is Cleaner Production?

Cleaner production is a phrase used to describe a preventive environmental strategy for industrial production that reduces risks to human health and the environment. The United Nations Environment Programme (UNEP) defines cleaner production as "the conceptual and procedural approach to production that demands that all phases of the life-cycle of a product or of a process should be addressed with the objective of prevention or minimization of short- and long-term risks to humans and the environment." UNEP's concept of cleaner production is similar to the concept of pollution prevention as defined today by the United States Environmental Protection Agency. Cleaner production applies to both products and processes. Cleaner products are those designed to reduce impacts throughout their entire life cycle, from raw material extraction to ultimate disposal of the product and packaging. Cleaner production processes conserve raw material and energy, eliminate toxic materials, and are adjusted, changed, or upgraded to reduce the generation of wastes and emissions.

Cleaner production is not an absolute state, but is continually evolving as new knowledge, improved technology, and changing attitudes are applied in the production and delivery of products and services.

Where did the concept come from?

The concept grew from efforts in Europe in the 1970s to promote "low- and no-waste technologies." In 1989, to assist developing countries in obtaining information on cleaner industrial practices, UNEP's Industry & Environment Programme established the Cleaner Production Programme to promote the transfer of technology. An advisory group adopted the phrase "cleaner production" because it suggested a more comprehensive approach.

What are the components of Cleaner Production?

Cleaner production includes several important components. Conventional discussion often lists six such components:

1. Waste Reduction. Because waste often is an indicator of inefficient materials use, cleaner production strives to reduce all waste to a minimum. Waste is defined quite broadly to include hazardous and solid wastes, liquid and gaseous wastes, waste heat, and off-spec or unmarketable product. The goal of cleaner production is zero waste discharge.

2. Non-Polluting Production. The ideal production processes take place in a closed loop with zero contaminant release. The use of toxic chemicals should be avoided where there are equally effective non-toxic substitutes. Where toxic chemicals are used, the elimination of spills, accidents, and fugitive releases is required. Release-preventing practices should be used in receiving, transfer, storage, and shipping operations, as well as in production processes.

3. Production Energy Efficiency. Cleaner production requires the highest levels of energy efficiency and conservation. Energy efficiency is determined by the highest ratio of energy consumption to product output. Energy conservation involves process heating and cooling, mechanical motion, lighting, room temperature management, transportation, and electronic monitoring and control.

4. Safe and Healthy Work Environments. Cleaner production strives to minimize the risks to workers from chemical exposure, radiation, physical hazards, ergonomic factors, work stress, fatigue, or unrewarding activities. Not only should the workplace be clean and safe, but the work processes should be appropriate to the skills and capacities of the workers. Work stations should be flexibly designed so that workers may modify them to achieve the highest level of comfort and productivity.

5. Environmentally Sound Products. The final product and all marketable by-products should be as environmentally appropriate as possible. Products should be designed to maximize the material-to-product ratio, minimize the use of toxic chemicals, and conserve the use of energy. Health and environmental factors must be addressed at the earliest point of product and process design and must be considered over the full product life-cycle, from production through use and disposal.

6. Environmentally Sound Packaging. Product packaging should be minimized wherever possible. Where packaging is necessary to protect the product, to market the product, or to facilitate ease of consumption, it should be as

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environmentally appropriate as possible. In designing packaging, degradability or ease of recycling and reuse are important criteria.

Why is Cleaner Production important?

Cleaner production reduces the costs of product liability, waste management, process operations, and occupational hazards while promoting worker and public health and environmental quality. Cleaner production is cost-effective, and cleaner products open up new, competitive markets.

How can Toxics Use Reduction promote Clean Production?

Toxics use reduction (TUR) can be one of the most effective elements in a cleaner production strategy because it focuses on reducing the use or waste of toxic substances within existing industrial processes. TUR planning provides information about sources and quantities of wastes, emissions, and other inefficiencies in production processes, and an accounting of their associated risks and costs. Improvements in efficiency and environmental soundness may be achieved through several TUR techniques:

- **Input substitution** — substitution of toxic raw materials with nontoxic or less toxic ones
- **Production process modification** — changes in the process that reduce toxic waste and emissions and improve energy and material efficiency
- **Finished product reformulation** — redesign of products to eliminate or minimize the use of toxic substances within the process and the product
- **Production modernization** — replacement or upgrading of production equipment and technologies to reduce toxic waste and emissions
- **Improvements in operation and maintenance** — improvements in housekeeping, systems, and control equipment to reduce waste and improve efficiency
- **In-process recycling of production materials** — closed loop recycling of substances, especially toxic ones, to decrease raw material requirements and waste

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Non-Cyanide Plating Processes

Today, many metal platers are seeking alternatives to traditional cyanide plating processes. Concerns over occupational health and safety, waste treatment costs, regulatory compliance requirements, and potential liability have encouraged process managers to investigate new, non-cyanide plating technologies.

Non-cyanide-based alternatives are available for cyanide-based copper, zinc, and cadmium plating processes. These substitute processes can reduce regulatory and reporting requirements, lower risks to workers, decrease environmental impact, and reduce corporate liability.

This fact sheet summarizes some viable alternatives to traditional cyanide plating methods. The alternatives presented are not all-inclusive, nor is one alternative recommended over another. The options listed are reasonably available and in most cases permit use of existing equipment with minor capital investment for modifications.

Cadmium Alternatives

Several non-cyanide plating finishes, including zinc, zinc alloy, and tin alloy, provide corrosion protection. These alternatives may be used in place of the toxic cadmium plating methods; the choice of alternatives depends on desired deposit characteristics.

General Considerations When Using Non-Cyanide Processes

- More than one non-cyanide process may be required to meet all the needs of a single facility.
- Process controls and cleaning practices must be maintained within tighter limits.
- Without the complexing ability of cyanide, periodic removal of iron and other potential contaminants may be required to assure deposit quality. Filtration is generally necessary when using non-cyanide processes.
- The color shades obtained in chromating over non-cyanide deposits do not always match those obtained with the same colors of chromates over cyanide deposits. Customers should be notified when it is important to segregate products with color shade differences.

- Some non-cyanide processes do not satisfactorily adhere to all surfaces and tend to become brittle at high temperatures.
- Alkaline non-cyanide processes generally provide more

Copper

Zinc

Cadmium

Zinc Alloy

Tin Alloy

ductile deposits for subsequent forming operations than do acid non-cyanide processes.

- Acid non-cyanide substitutes usually incorporate more organic brightening agents than alkaline non-cyanide substitutes. In both acid and alkaline non-cyanide processes, higher levels of organic or non-organic brightening agents provide a more cosmetically appealing result. However, chromating may be more difficult with high levels of brighteners, particularly organic brighteners, as a deposit surface film.
- Acid substitution processes require an appropriate (e.g., plastic) liner.

Environmental, Health, and Safety Considerations

Examination of alternatives should include consideration of environmental and health and safety tradeoffs at all stages of production, including raw materials acquisition, processing, and recycling or disposal.

- Material safety data sheets must be reviewed and vendors should be questioned about the presence of ammonia, formaldehyde, or other agents in some substitute chemistries that may present worker or environmental concerns and which may require redirecting of waste streams for treatment compliance.

Alternatives Matrix

The matrix on the following pages provides comparative information on a wide range of different options. Information on product quality and process parameters is provided for a range of zinc, cadmium, and copper alternatives. These parameters include corrosion protection, finish appearance, color, ductility, plating uniformity, and other process considerations.

Cyanide Process	Alternative	PRODUCT QUALITY			
		Corrosion Protection	Finish Appearance	Chromate Colors	Ductility
Zinc ¹	Zinc Alkaline	(+) Good, greater protection in difficult to rinse areas	(+) Good brightness	Full line available	(+) Good, may be reduced at higher thickness
	Zinc Acid Chloride	(+) Good, but less protection in difficult to rinse areas	(+) Excellent brightness and leveling	Full line available	(-) Higher brightener levels may reduce ductility (+) little hydrogen embrittlement
Cadmium ¹	Cadmium Neutral or Acid Sulfate	(+) Good	(+) Satisfactory	Full line available	(+) Good, little hydrogen embrittlement
	Cadmium Acid Fluoborate	(+) Good	(+) Satisfactory	Full line available	(+) Good, little hydrogen embrittlement
	Zinc Nickel Alkaline	(+) Excellent with chromate conversion coating	(+) Good	Specialized chromates: bronze, yellow, iridescent, black	(+) More ductile than acid zinc
	Zinc Nickel Acid	(+) Good	(+) Good brightness at higher efficiency	Specialized chromates: bronze, yellow, iridescent, black	(-) Less ductile due to higher brightener levels
	Zinc Cobalt Acid	(+) Good	(+) Excellent (+) Provides deep uniform black without use of silver	Specialized chromates: bronze, yellow, iridescent, black	(+) Fair, lower hydrogen embrittlement than alkaline
	Zinc Cobalt Alkaline	(+) Good	(+) Provides deep uniform black without use of silver	Specialized chromates: bronze, yellow, iridescent, black	(+) Better than acid bath
	Zinc Iron Acid or Alkaline	(+) Good, not recommended for high temp. applications	(+) Provides deep uniform black without use of silver	Black, others limited based on bath conditions	(+) Good
	Tin Nickel Acid or Near Neutral	(+) Good resistance to corrosion and tarnish	(+) Can be decorative in appearance	N/A	(+) Good
	Tin Zinc Acid, Alkaline or Neutral	(+) Good with chromate applied (+) Does not undergo bimetallic corrosion	(-) Fair	Limited to yellow	(+) Excellent (soft deposit)
Copper	Copper Alkaline	N/A	(+) Good appearance	N/A	(+) Good
	Copper Acid Sulfate or Fluoborate	N/A	(+) Good appearance (+) Excellent leveling	N/A	(+) Good to Excellent
	Copper Pyrophosphate	N/A	(+) Good, fine grained and semi-bright	N/A	(+) Good

- Notes: 1. Alkaline and acid zinc may also be used as cadmium cyanide plating substitutes.
2. N/A = Not Applicable

Alternative	PROCESS		GENERAL COMMENTS
	Plating Uniformity	Process Considerations	
Zinc Alkaline	(+) Good, uniform in high and low density areas (+) Good throwing power	(-) Narrow optimum operating range of bath parameters	(-) Lower conductivity than acid zinc (+) Better for some forming operations (-) Harder to plate on cast iron and carbonitrided steel
Zinc Acid Chloride	(-) Variable with current density	(-) Liners necessary in steel or porous tanks (+) High cathode efficiency at high current densities (-) Agitation required	(+) Higher conductivity results in energy savings (-) Bleedout of entrapped plating solution may limit use for complex parts (+) Plates readily on cast iron and carbonitrided steel
Cadmium Neut./Acid Sulfate	(-) Poor throwing power	(-) Liners required for acid, preferred for neutral	(-) High toxicity, low discharge limits for cadmium; not preferred toxics use reduction (TUR) option
Cadmium Acid Fluoborate	(-) Poor throwing power	(+) High cathode efficiency at high current densities (+) Good stability	(+) Good data on use available - widely used in barrel plating (-) High toxicity, low discharge limits for cadmium; not preferred TUR option
Zinc Nickel Alkaline	(+) More uniform thickness and alloy distribution than acid Zn Ni (+) Good throwing power	(-) Chiller required to maintain optimum temperature (-) Slower plating speed than acid Zn Ni (+) Chemistry similar to alkaline Zn	(+) Good corrosion properties maintained after forming and heat treating (-) May contain chelators
Zinc Nickel Acid	(-) Poor thickness distribution, alloy variation from high to low current density	(-) Requires additional inert anodes and segregated rectification (+) Faster plating speed than alkaline Zn Ni	(+) Good corrosion properties maintained after forming and heat treating (-) May contain ammonia or chelators
Zinc Cobalt Acid	(-) Poor throwing power (-) Variable with current density	(+) Good plating speed (+) High cathode efficiency	(+) No silver required for black chromating (-) May contain chelators
Zinc Cobalt Alkaline	(+) More uniform than acid ZnCo	(-) Lower efficiency than acid ZnCo	(+) No silver required for black chromating (-) May contain chelators
Zinc Iron Acid or Alkaline	(+) Good throwing power	(-) Iron content must be controlled to prevent blistering	(+) No silver required for black chromating (-) May contain chelators
Tin Nickel Acid/Near Neutral	(+) Deep throwing power	(-) Chiller required (-) Lined tanks recommended	(+) Good hardness (between Ni and Cr) and wear resistance, low contact resistance (+) Ability to retain oil film for lubrication
Tin Zinc Acid, Alkaline or Neutral	(-) Poor throwing power (+) Excellent covering power	(-) Chiller required	(+) Excellent solderability properties
Copper Alkaline	(+) Better throwing power than cyanide	(+) Operating pH range 8.0 to 10.5	(+) Can be used as heat treat maskants (+) Less corrosive (+) May be used as strike bath
Copper Acid Sulfate or Fluoborate	(-) Less macrothrowing power than alkaline (+) more microthrowing power than alkaline	(-) Lined tanks and appropriate anode baskets required (+) Fluoborate allows use of higher current densities	(+) Good use data available (-) Corrosive on coatings and some substrates
Copper Pyrophosphate	(+) Good throwing power	(+) Operating pH 8.0 to 8.8 (-) More sensitive to organic contaminants than acid Cu (-) May require longer plating time	(+) May be used as strike bath (-) May contain ammonia



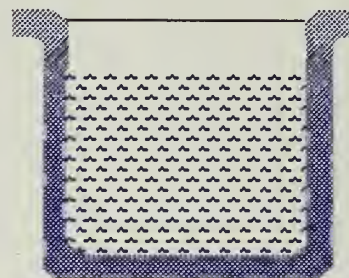
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This fact sheet was compiled using the most current information available at the time of preparation. Users are advised to check with suppliers regarding specific criteria, applications, and environmental, health, and safety concerns.

Technical guidance for this fact sheet was provided by Vincent G. Piekunka. Information was also drawn from "Making It Work: Non-Cyanide Plating Alternatives," prepared for the Massachusetts Toxics Use Reduction Institute by Mabbett & Associates, Inc.

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce.





Alternatives to Solvent-Based Coatings

Substitute coatings are available that reduce or eliminate the use of VOC-containing solvents in the application of coatings and can decrease environmental impact, regulatory and reporting requirements, worker safety concerns, and corporate liability.

This fact sheet summarizes several opportunities for substitution in a variety of industries that apply coatings, including but not limited to original equipment manufacture, refinishing, and industrial and architectural maintenance.

- Water-based coatings
- High solids coatings
- Powder coatings
- Radiation-cured coatings
- Supercritical fluid spray application
- Surface-coating-free materials

The composition of the coatings alternatives and some use considerations are described below. An alternatives matrix on pages 3 and 4 provides comparative information on each alternative, including operational, cost, and quality considerations. Articles, guides, and industry case studies are listed on pages 5 and 6.

The options presented are not all-inclusive, nor is one option recommended over another. Examination of alternatives to solvent-based coatings should include thorough consideration of environmental and health and safety tradeoffs at all stages of production, including raw materials acquisition, processing, and recycling or disposal, as well as any new or unknown hazards in the alternative materials.

Product or Chemical Substitution Alternatives

Water-based coatings

Water-based coatings or water-borne coatings, are similar in composition to conventional solvent-based coatings, except that water supplements or completely replaces the solvent. They usually contain up to 80% water with small

amounts of solvent to facilitate dispersion of the resin. There are three main types: water soluble or water-reducible coatings; colloidal or water-solubilized dispersion coatings; and, most commonly used, emulsion (latex) coatings.

Water-based coatings have been successfully applied to metal, wood, plastics, concrete, paper, and leather, and formulations are available for many specific applications. Application technology is generally comparable to that of conventional solvent-based coatings. Overspray is easily recovered and reused, and uncured coating can be cleaned from equipment with water. Some formulations or substrates may require special pumps and piping to prevent corrosion from water in the formulation. Some coatings are applied by electrodeposition for corrosion resistance and coating of hard-to-reach areas. Most water-based coatings are sensitive to surface conditions, temperature, and humidity. Longer drying time is needed unless a drying oven is used. Some resins may cause water spotting; additives to control water spotting may present worker safety hazards.

High solids coatings

High solids coatings have a lower VOC concentration and higher resin concentration than conventional solvent-based coatings. Solids content is typically 50-70% but can be as high as 100%. Formulations consist mainly of resins (usually of low molecular weight), pigments, extenders, and additives with a solvent carrier, and include saturated polyesters, alkyds, acrylics, polyurethane, and epoxies.

High solids coatings can be applied to wood, plastic, and metal. Their viscosity and physical properties are similar to those of conventional coatings, and they can be applied with some types of conventional equipment, although higher viscosity coatings require special spray equipment. High solids coatings have greater transfer efficiency and reduce paint wastes. Careful surface preparation and worker retraining in application techniques are necessary. Some formulations contain chlorinated solvents as substitutes for VOC ozone precursors; the toxics use reduction impact of these products should be considered in comparison to conventional solvent-based coatings and other alternatives.





Powder coatings

Powder coatings contain little or no solvent. They are composed of a finely pulverized powder of thermoplastic or thermosetting resins with a built-in curing agent mixed with pigments. Use of a reactive resin in dry powdered form eliminates the need for solvent. The powder is applied with an electrostatic gun or in a fluidized bed, and then melted or reacted to form a coating. **Thermoplastic powders**, applied in thick coatings, include cellulose acetate butyrate, polyesters, and polyamides. **Thermosetting powders**, applied in medium-thickness coatings, include epoxy resins, acrylics, and polyesters. Current technology permits successful application to plastics, glass, ceramics, wood, and metal.

Powder coatings produce a durable, high quality finish with good corrosion resistance. Their higher installation and unit costs are offset by savings in maintenance, materials, labor, energy, and waste disposal. Some ingredients, such as pigments and curing agents, may present skin contact or dust inhalation hazards. Precautions are needed to reduce the potential for the powders to form explosive mixtures with air.

Radiation-cured coatings

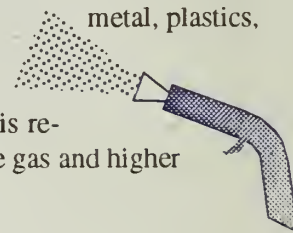
Radiation-cured coatings contain little or no solvent. In place of solvent are reactive molecules that polymerize when activated by high-energy radiation such as ultraviolet (UV) light, infrared light, or an electron beam (EB).

Radiation-cured coatings are applied to plastics, wood, paper, and metal. They have a considerably shorter curing time and give the same finish regardless of environmental conditions. UV- and EB-cured coatings are currently most commercially applicable. Flat materials cure best, but coating of three-dimensional objects is possible. Improvements in lamp systems now allow UV curing of pigmented coatings.

Acrylate materials (e.g., acrylonitrile), present in most radiation-cured coatings, are known skin and eye irritants and probable carcinogens; high exposures can cause collapse and death. Protective equipment is important in preventing skin and eye contact. Toxicity testing by a supplier and user panel is underway, and a family of vinyl ether substitutes with lower toxicity profiles has been developed, but performance information is incomplete.

Supercritical fluid spray application

Supercritical fluid spray application allows substitution of supercritical carbon dioxide for up to two-thirds of conventional solvents concentration in spray-applied coatings, reducing VOC emissions by 30-70%. The proportioning and supply (UNICARB) system from Union Carbide mixes supercritical CO₂ solvent with coating concentrate and supplies the material to a specially designed spray gun. The CO₂ solvent is compatible with high-molecular-weight resins and existing painting facilities and procedures. Supercritical fluid spray application may be used to coat metal, plastics, and wood. The applied coating has a higher viscosity that allows thicker coatings without runs or sags. Care is required in working with high-pressure gas and higher operating temperature (100-150°F).



Surface-coating-free materials

Surface-coating-free materials that are corrosion- and UV-resistant may in some situations be effective substitutes for materials that require coating. Currently available surface-coating-free materials include plastics, aluminum, titanium, and other metals. Many others, including cement-bonded particle boards, pultruded products from fiberglass-reinforced plastic, uncoated metals, weathering steel, and polymer film coatings, are under development for a wide range of industries.

Use of these materials where feasible eliminates VOC emissions and worker exposure from painting operations. These materials are often more expensive initially, although the initial increased expense may be offset by reduced maintenance or eliminated recoating costs.



References

Resources listed are available from the publisher and may be viewed at the Technology Transfer Center of the Massachusetts Toxics Use Reduction Institute. To order U.S. EPA publications, call EPA's Pollution Prevention Information Clearinghouse (703) 821-4800. Information for contacting other publishers is available from the Institute.

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Industry Case Studies

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- Environmental Research Briefs*. EPA Risk Reduction Engineering Laboratory, Cincinnati, OH. Series describing facility site assessments and recommended waste minimization opportunities, including savings, implementation costs, and payback. Product or chemical substitution options for painting operations are described for manufacturers of the following products:
- Military furniture:** EPA/600/S-92/017 June 1992
- Sheet metal cabinets and precision metal parts:** EPA/600/S-92/021 May 1992
- Motor vehicle exterior mirrors:** EPA/600/S-92/020 May 1992

Please turn page.



Industry Case Studies (continued)

Environmental Research Briefs (continued)

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Overview of Machining Fluids and Aqueous Cleaning with Pollution Prevention Opportunities

In the machining of metals, fluids are used as lubricants, chip removers, rust inhibitors, and coolants. A variety of machining fluids are used based on compatibility with the metal and the machining process.

After a part has been machined it often must be cleaned to ensure the success of further processing steps (such as electroplating). Historically firms have cleaned work-pieces in degreasers containing chlorinated solvents. Under the Montreal Protocol companies were required to phase-out production of 1,1,1-TCA (trichloroethane) and chlorofluorocarbons (e.g., CFC-113) by 1995. Also, taxes and disposal costs of these chlorinated solvents are increasingly prohibiting their use. Water-based cleaners will most likely be favored over the many possible replacements for chlorinated solvents.

This fact sheet presents the new challenges that companies face in reducing their reliance on chlorinated solvents. It describes types of machining fluid and suggestions for selecting and maintaining fluids. Also included is a description of aqueous cleaning technologies for firms that are considering adopting them and suggestions for firms trying to improve their existing aqueous cleaning process. The fact sheet provides insight into the relationship between machining fluids and aqueous cleaning.

Selection Processes

Large firms may employ a lubricating engineer to select the best machining fluid for a given application, however smaller firms are often less systematic. When selecting a machining fluid, it is important to consider not only how well it performs, but also the ease of removing and recycling the fluid, and the worker health and safety impacts of that fluid. By improving the method of selection and application, fluid purchase and disposal costs can be decreased while reducing the load to the cleaning system.

For aqueous cleaners there is no complete information regarding a cleaner's effectiveness at removing a specific contaminant and often product information sheets overstate the cleaner's capabilities. These factors make selecting an appropriate aqueous cleaner a challenging task. Recommendations for effective cleaning formulations for specific applications can be obtained from the Toxics Use Reduction Institute's (TURI) Surface Cleaning Lab,¹ vendors or literature case studies. Bench-scale testing may be necessary to further evaluate the recommendations.

Machining Fluids

Machining fluids can be categorized by percent mineral oil content and percent and type of additives used as lubricants, emulsifiers, rust inhibitors and biocides. General formulations of machining fluids are given on product information sheets and Material Safety Data Sheets (MSDSs). Machining fluids are often divided into three categories: cutting oils, water-soluble fluids, and paste or solid lubricants.

Cutting Oils

Cutting oils are mineral oils used alone or compounded with polar additives (such as vegetable oil) and/or chemically-active additives. The mineral oils used are typically paraffinic (straight-chain hydrocarbon base), or naphthenic (ring-structured hydrocarbon base). Naphthenic oils are more widely used because they have a much higher solubility for additives. There are two classes of cutting oils: inactive and active. Inactive cutting oils are mineral oils compounded with chemically inactive additives which provide increased lubricity. Active cutting oils are mineral oils or fatty mineral oil blends that contain sulfur, chlorine or phosphorus in an active form which reacts with the metal (see Table 1).

Water-Soluble (Water-Miscible) Fluids

Water-soluble fluids are primarily used for high-speed machining to prevent thermal distortion of the tool and work-piece. For machining that is high-speed chip making, the oil concentrate is usually blended 1 part with 20 to 30 parts water. For many grinding operations where a lighter fluid with better cooling properties is desired, the ratio of oil to water may be from 1:40 to 1:50. The three types of water-soluble fluids are: emulsifiable oils, synthetic (chemical) fluids, and semisynthetic (semichemical) fluids. Synthetic fluids consist of inorganics and/or other materials dissolved in water. They contain no mineral oil. Semisynthetic fluids are a combination of synthetics and emulsifiable oils (see Table 1).

Paste and Solid Lubricants

Grinding wheels are sometimes impregnated with solids possessing lubricating qualities. In special cases grinding wheels are treated with sulfur to produce a cooling action in wet grinding. Often grease sticks are externally applied to grinding wheels and solid waxes are used on grinding wheels, sanding disks or belts, and band or circular saw blades. Other solids commonly used as heavy-duty lubricants are molybdenum disulfide, tripoli, graphite, mica, talc, glass, pastes, and soaps.^{2,3}



Table 1. Types and Characteristics of Machining Fluids

	Type	Characteristics and Uses
Inactive cutting fluids	Straight mineral oils	Used in light duty operations that require low levels of cooling and lubrication; if kept clean, they can be reused indefinitely; lower in cost than compounded oils
	Fatty oils	Most common types are lard and rapeseed oil; high anti-friction properties but poor anti-weld characteristics; have a tendency to emit unpleasant odors
	Compounded cutting oils	Made by blending mineral oils with polar additives and/or chemically active additives
	Fatty-mineral oils	Straight mineral oils blended with up to 40% fatty oil
	Inactive extreme-pressure (EP) additives	Additives such as chlorine, sulfur or phosphorus added to mineral or compounded oils for machining applications where forces are high
Active cutting fluids	Fluids containing sulfur additives	Contain sulfur additives that form metallic sulfide films which act as solid films up to 1300°F; may stain aluminum, copper, brass, bronze, and magnesium; nonferrous metals less likely to be stained
	Fluids containing chlorine additives	Ferrous chloride film that forms when chlorine reacts with ferrous workpieces or HSS (high strength steel) tools; low shear strength reduces friction at temperatures up to 750°F
	Fluids containing phosphorus additives	Phosphorus additives used as friction and wear reducers; will not stain ferrous or nonferrous workpieces
Emulsifiable oils	Emulsifiable mineral oil	Suspension of mineral oil made by blending the oil with an emulsifying agent; emulsifiers break the oil into minute particles and keep the particles dispersed in water for a long period of time; bactericides (commonly nonphenolic compounds) are used to control the growth of bacteria, algae, and fungi; phenolics may be used when disposal is not a concern
	Extreme-pressure emulsifiable oils	Sometimes referred to as heavy-duty soluble oils; contain sulfur, chlorine, or phosphorus; may also contain some fatty oils to increase lubricity
Synthetic fluids	True solution fluids	Chemical solutions containing rust inhibitors, sequestering agents, amines, phosphates, borates, glycols or ethylene oxide condensates; have a tendency to leave a residue of hard or crystalline deposits that are formed when water evaporates
	Surface-active chemical fluids	Fine colloidal solutions of organic or inorganic materials dissolved in water; wetting agents are usually added to provide moderate lubricity; have low surface tensions; usually contain rust inhibitors; when they dry onto a work-piece they usually leave a powdered residue
	EP surface-active chemical fluids	Similar to surface-active fluids but contain EP additives such as chlorine, sulfur, and phosphate to give the fluid extreme pressure lubrication qualities

Aqueous Cleaner Components

Aqueous cleaner chemistries are complex and cleaning formulations vary greatly. Aqueous cleaners use water as the primary solvent. Formulations may be divided into categories by what combination (types and percent concentration) of builders, additives, and surfactants are present in a formulation, however formulators do not typically disclose this information due to its proprietary nature. MSDSs contain basic properties (pH, flash point, etc.) of the cleaner and product information sheets include information such as substrate compatibility. Surfactants are combined with builders and additives such as pH buffers, rust inhibitors, chelating agents,

and saponifiers. These agents provide multiple degrees of freedom in formulating, blending, and concentrating. They also provide useful synergistic effects. A brief description of each component and its function follows.

Builders

Builders are the alkaline salts in alkaline cleaners. An aqueous cleaning formulation usually includes two or more builders that serve many functions which depend on the type of builder used. There are three main groups: phosphates, silicates, and carbonates.

Phosphates soften water, eliminating the flocculent



precipitate caused by calcium, magnesium and iron. They also act as a soil dispersant, a buffer, and a source of alkalinity. Silicates provide alkalinity, prevent redeposition of soil by keeping it suspended, provide detergency, and act as inhibitors protecting metals such as zinc and aluminum from other alkaline salts.

Carbonates are an inexpensive source of alkalinity and act as buffers in solution. Carbonates can also be an adsorbing media for the liquid components of the cleaner when the cleaner is in a powdered form. Two other substances that are used as builders in aqueous cleaning formulations are hydroxides and borates. Hydroxides are a relatively inexpensive source of alkalinity. Borates act as buffers and provide some detergency and metal protection.⁴

Additives

Additives are organic or inorganic compounds that provide many functions including additional cleaning or surface modification. They also soften water and complex or tie up metal ions. The three main types of additives are chelating agents, rust inhibitors, and sequestering agents.

Chelating agents solubilize metal salts by forming chemical complexes. Chelating agents are sometimes used as builders in place of phosphates to eliminate the possible problem of eutrophication of water bodies.

Inhibitors minimize the negative effects alkaline cleaners may have on certain metal substrates. They prevent rusting of the part being cleaned and of the cleaning equipment. Inhibitors are found in high pH cleaners to prevent the cleaner from attacking non-ferrous metals. Low pH cleaners do not usually contain inhibitors. Inhibitors may be used in the wash stage of a single stage cleaning operation or in the rinse phase of a multiple stage cleaning process. Inhibitors may deposit a film on a part which may interfere with future processing or increase the difficulty of rinsing.⁵

Sequestering agents combine with heavy metal ions, (calcium and magnesium) in hard waters to form molecules that can no longer react. Sequestering agents also prevent salts from recontaminating parts.

Surfactants

Surfactants are organic compounds in aqueous cleaning formulations that provide solubilization, emulsification and wetting. Because of their unique chemical characteristics, surfactants lower the surface tension of water. This enables the detergent to wet small areas otherwise inaccessible to water. The hydrophobic portion of the surfactant molecule may react with the machining fluid and remove it from the part.

There are four main types of surfactants: nonionic, anionic, cationic and amphoteric. The two main types used in aqueous cleaning are nonionics and anionics.

Nonionic Surfactants

- most widely used in metal-cleaning
- useful over a wide range of pH
- effective at solubilizing nonpolar soils
- effectiveness is temperature dependent
- no charged group
- low-foaming

Anionic Surfactants

- most widely used in the surfactant industry due to their low production costs
- not as commonly used in metal cleaning due to foaming
- work effectively in immersion applications where foaming is not a factor
- effectiveness not temperature dependent
- negatively charged end
- can solubilize polar soils

Cleaning Equipment

Process equipment used with aqueous-based cleaners can be divided into three categories: cleaning, rinsing, and drying. The washing equipment may be immersion, spray, or ultrasonic.

Immersion

In an immersion system the parts are immersed in a solution and some form of agitation adds the energy needed to displace and float away contaminants. Soil is removed from the metal surface by a combination of the aqueous cleaner and the currents in the solution. The currents are created by heating coils or by mechanical action such as rotation, agitation, or circulation. The method of agitation selected can be tailored to part size and geometry.

Immersion

Advantages	Disadvantages
Can use existing vapor degreasing equipment with some simple changes Will flush out chips Cleans complex parts and configurations Usable with parts on trays Simple to operate	Difficult to automate May require proper part orientation and positional changes while in solution



Spray Washing

In the spray washing method, parts are sprayed with a solution at various pressures from 2 psi to more than 400 psi. Low pressure spray washers may be small, manually operated models which may require some hand scrubbing. The higher pressure spray washers deliver more mechanical action to help remove soils from metal surfaces. Spray cleaners are prepared with low foaming detergents which may be less effective chemically than those used in immersion cleaners. Their effectiveness is due to the increased mechanical action. Although spray cleaning is effective on most parts, certain configurations have soiled areas (such as the interior of an automobile tail pipe) that are inaccessible to the spray stream. In these instances, immersion cleaners are more effective. Optimization of nozzle design parameters such as spray pattern, drop size and formation, pressure/velocity, and volume may have a major impact on effectiveness.

Spray Washing

Advantages	Disadvantages
High level of cleanliness Relatively inexpensive Will flush out chips Can process a high volume of parts at one time Simple to operate Good for continuous processes	Not effective in cleaning complex parts Can process a high volume of parts at one time with blind areas Not effective on very small or light weight parts Contaminants containing fatty oils and/or glycerides may react with alkaline cleaners causing foaming

Closed Loop Aqueous Cleaning

Some firms switching to aqueous cleaning do not have a water discharge permit, which may be required for disposal of aqueous cleaning solutions. When aqueous cleaner baths are spent and discharged, they can cause problems with the normal operation of a wastewater treatment system. This makes closed loop filtration systems a necessity. These systems also alleviate some of the water, sewer, and cleaner costs.

Closed loop aqueous cleaning involves the removal of contaminants from the cleaner bath. The useful life of the cleaner is extended and the quantity of waste disposed is minimized. A variety of methods exist for removing contaminants from aqueous solutions. Methods selected for a particular application are often chosen on the basis of contaminant size. Particulate matter may be removed using settling tanks, chip baskets, and media or canister filters. Tramp oils are removed using skimmers and coalescers. Microfiltration can be used to remove particulate matter, tramp oils, and greases and ultrafiltration is effective at removing emulsified oils.⁶

Rinsing

The rinse step in aqueous cleaning is crucial. There are immersion, ultrasonics, and spray rinse systems. The temperature of the rinse water needs to be tailored to the substrate being rinsed. For example, rinse water for brass can not be higher than 150°F to prevent etching. Also, carbon steels need to be cold rinsed to prevent rusting because rusting is a temperature dependant chemical reaction. Water hardness is also a concern for rinse water because hard water will cause spotting during drying.

Drying

There are a number of drying systems available:

- compressed air or blower
- heated compressed air
- infrared lamps
- convection ovens
- vacuum ovens
- centrifugal dryers

The drying temperature should be set for the material being dried because high temperatures may adversely effect some substrates.



Ultrasonics

In this cleaning method ultrasonic waves are generated in the cleaning bath which cause tiny bubbles to form and collapse at the surface of the part. This is known as cavitation. Process design requires caution to insure that cavitation erosion of the parts' surfaces is not a problem.

Ultrasonics

Advantages	Disadvantages
Highest level of cleaning Can be automated Cleans complex parts and geometries	Noise may be a nuisance Cannot handle hard soils May damage soft metals Parts need to be arranged so that all surfaces wet



Industry Case Studies (continued)

Environmental Research Briefs (continued)

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Opportunities for Pollution Prevention

Operating and process modifications may be employed to decrease costs and the environmental impact of these processes.

Machining Fluids

- Explore technologies that do not use machining fluids such as: electrical discharge machining; waterjet, plasma arc, or laser cutting; electrochemical machining; electromagnetic forming; and coated tool piece machining.^{7,8}
- When selecting a machining fluid, consider other processes such as parts cleaning, cleaning bath extension, and machining fluid life extension and recyclability. Some distributors will work with you to reformulate an existing oil to make it more compatible with other processes.
- Explore reducing the amount of machining fluid used for a given application. There are firms that will monitor tool and work pieces to prevent damage while companies explore reducing their machining fluid use.
- The method of machining fluid application may be a source of inefficiency. Use automated spray nozzles and counters where possible.⁹ When selecting spray nozzles consider the spray pattern, angle, and pressure, and the configuration of the nozzles.
- Vegetable-based lubricants should be used when possible because they are produced from renewable resources and pose less environmental impact.
- For soluble fluids, explore alternatives to biocides such as micro or ultrafiltration that eliminate the growth of bacteria and the negative health effects associated with biocides and bacterial growth. This also eliminates the potential need to dispose of these fluids as hazardous waste.¹⁰
- Remove contaminants continuously using any number of mechanical separators such as coalescers, skimmers, and sump cleaning units. Also, maintain the proper pH and concentration to increase the useful life of the fluid.¹¹
- Perform an analysis on the water used as mix water to insure that the water hardness and total dissolved solids content will not interfere with the fluid performance. Deionization, distillation, or reverse osmosis may be desirable.
- Use the fewest number of fluids possible. This will help when segregating waste streams for recycling and it will simplify machining fluid record keeping.¹² Cleaning issues are also simplified when fewer fluids are used.

Aqueous Cleaning

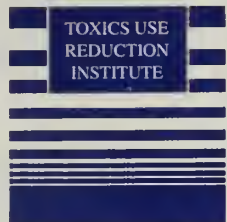
- Knowledge of the contaminants on a part results in a more educated decision about how to clean it. This knowledge could eliminate trial-and-error cleanings.
- For firms that source-out work, assess whether parts are contaminated during shipping and eliminate cleaning steps that must be repeated after shipping. Also, eliminate cleaning steps that provide incomplete removal of contaminants or cleaning steps that result in hard water stains. The vendor that receives the parts may have a more difficult time cleaning the parts.
- Dump wash baths only when necessary. Tests such as pH, conductivity, turbidity, and refractometry are available to determine when a bath is spent. Conductivity and pH tests indicate the concentration of the cleaning formulation while refractometry and turbidity indicate the loading of contaminants in the bath.
- Use a counter-current rinse system to decrease water usage. These systems include two or more rinse tanks in series. The work-pieces move in the opposite direction than the water flow.
- When changing a cleaning bath use rinse water as make-up for the new wash bath.
- Drying may be the most expensive and energy intensive step in an aqueous cleaning process. Firms should determine an acceptable level of dryness and avoid over-drying.
- In non-precision applications use filtration techniques such as coalescing and cartridge filters to extend cleaner and rinse bath lives. These filters remove non-emulsified oils and particulate matter.
- Install a microfiltration system to remove all contaminants (except for emulsified machining fluids). For cleaners that do not emulsify machining fluids microfiltration may extend the cleaner and bath lives indefinitely.
- Ultrafiltration removes emulsified oils. These systems are useful for precision cleaning applications and applications where it is desirable to discharge effluent as non-regulated waste. Savings are realized in water, sewer and cleaner costs.



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9. The Norwood Stamping Co., Inc. has reduced their use of machining fluids by greater than 50% using spray nozzles and counters. This also reduced the contaminant load on the aqueous cleaning system.
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11. Environmental Services Division, State of Michigan, "Ten Ways to Reduce Machining Coolant Costs," In Office of Pollution Prevention, Ohio Environmental Protection Agency, Metal Working Fluids Pollution Prevention Information Packet, September 1995.
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Surface Cleaning

What is Surface Cleaning?

Surface cleaning or degreasing is the removal of contamination, or unwanted material, from a surface. Cleaning may be necessary for successful part performance in subsequent operations or may simply be performed for aesthetic reasons. In many industries, cleaning and degreasing of surfaces has traditionally been accomplished by the use of chlorinated solvents in vapor degreasers or immersion systems. The chlorinated solvents most commonly used for metal cleaning include: 1,1,1-trichloroethane (1,1,1-TCA), trichloroethylene (TCE), perchloroethylene (PERC), dichloromethane (methylene chloride or METH) and chlorofluorocarbons (CFCs). Chlorinated solvents are effective cleaners and, in the past, have been considered "safe" to workers because they are nonflammable.

Due to concern over the ozone layer, photochemical smog and worker health, increasingly strict environmental regulations have been promulgated on the use of chlorinated solvents making traditional chlorinated solvent cleaning a process of the past. For many companies changing from a proven process to a new technology is a challenging task. Some alternatives presented as "perfect" solutions are found to be ineffective cleaners, too expensive, or present safety hazards. Knowledge of cleaning needs and cleaning options will aid in selecting the most cost effective and technically feasible solution without compromising worker health and safety or environmental protection.

TURI's Surface Cleaning Laboratory assists companies in matching specific cleaning needs with appropriate chemistry and process combinations.

To learn more about the Lab, please call (508) 934-3249 or visit the web site at <http://www.cleaning.org>. Services are free-of-charge to Massachusetts companies.

To find more information on cleaning alternatives, visit **TURI's Technology Transfer Center**, a clearinghouse of information. Reference services are available.

How are Cleaning Needs Defined?

The first and most important part of the search for an alternative is defining cleaning needs. Here are a few basic steps to follow.

Step 1: What are the parts? Define the parts to be cleaned. (e.g., materials of construction, type of surface, size and geometry)

Step 2: What are the contaminants? Identify the contaminants to be removed. (e.g., petroleum-based oil, water-based oil, vegetable-based oil, grease, wax, flux, dirt, salts.)

Step 3: Who is applying the contaminants to the parts? Minimizing the amount of or switching to an "easy to clean" contaminant will ease the cleaning load and difficulty. If suppliers are applying the contaminants, work with them to use less contaminant and find alternatives to "hard to clean" contaminants. (e.g., A company eliminated their entire cleaning operation by working with their supplier who now uses a vanishing oil.)

Step 4: Why are the parts being cleaned? Spend some time with this one. Don't be satisfied with the answer "because they've always been cleaned". Companies have saved money by eliminating unnecessary cleaning steps.

Step 5: What are the cleaning requirements? If cleaning must be done, it is necessary to know to what degree. This may be the most difficult step. Consider what happens to the parts following cleaning.



What are the Alternative Cleaning

Once cleaning needs have been assessed, evaluation of the alternatives can begin. Following are brief descriptions of the most popular alternatives.

Water-based cleaning, aqueous and semi-aqueous, is a widely applicable alternative to solvent cleaning.

Aqueous Cleaning

In some applications, hot water alone may be sufficient to clean parts. Others may require a wash, rinse, and dry cycle. When a detergent is required, synthetic detergents and surfactants are combined with special additives such as builders, pH buffers, inhibitors, emulsifiers, deflocculants, complexing agents, and anti-foaming agents. These agents provide multiple degrees of freedom in formulating, blending, and concentrating, and also provide useful synergistic effects.

Process equipment often used in aqueous cleaning is immersion, pressure spray or ultrasonic depending on the application. In immersion cleaning the parts are immersed in a cleaning solution and some form of agitation and/or heat is added to supply the energy needed to displace and float away contaminants. Immersion cleaning is relatively simple to operate and will flush out chips.

In pressure spray washing parts are cleaned with a solution sprayed at a pressure anywhere from 2 psi (pounds per square inch) to 400 psi. The higher spray pressure delivers more mechanical action to help remove soils from metal surfaces. Spray cleaners are prepared with low foaming detergents which are not as chemically effective as those used in immersion cleaners, but are still effective because of the increased mechanical action. Although spray cleaning is effective on most parts, certain configurations, such as the interior of an automobile tail pipe, have soiled areas that are inaccessible to the spray cleaning solution. In these instances, immersion cleaners are more effective.

The ultrasonic method combines water, a detergent and high frequency sound waves to provide the agitation. Ultrasonic cleaning uses sound waves in the 20 to 50 KHz range to provide cavitation bubbles in water. The mechanical effect of the ultrasonic energy helps to dissolve and displace particles from the surface.

Semi-Aqueous Cleaning

Semi-aqueous cleaners are made of natural or synthetic organic solvents, surfactants, corrosion inhibitors, and other additives. Water is used in some part of the cleaning process (washing and/or rinsing), hence the name, semi-aqueous. There are two types of semi-aqueous cleaners, water-immiscible and water-miscible. The water immiscible types, or emulsion cleaners, are a mixture of a non-water-soluble solvent, an emulsifying surfactant and water. Some common water-immiscible, semi-aqueous cleaners are terpenes, high-molecular-weight esters, petroleum hydrocarbons, and glycol ethers. The water-miscible types use water as a filler to reduce volatile organic compound (VOC) emissions. Some common water-miscible, semi-aqueous cleaners are low-molecular-weight alcohols, ketones, esters, and organic amines. Semi-aqueous cleaners are non-ozone-depleting but they may contain VOCs. Concerns with the use of semi-aqueous cleaners include aquatic toxicity, human health effects, and flammability, depending on the concentration of water. Semi-aqueous cleaning is most often accomplished in immersion or ultrasonic systems.

Carbon Dioxide Blasting

Carbon dioxide (CO₂) technology begins with the conversion of liquid CO₂ into solid CO₂. There are at least three carbon dioxide technologies in use: CO₂ snow, CO₂ pellet, and fragmented CO₂. In all forms, the cleaning action of the CO₂ is the same. As the material impacts the surface to be cleaned, it sublimates, returning to the gaseous state. The cleaning occurs as the sublimation causes turbulence on the surface and lifts the contaminants away. The contaminants and the CO₂ gas are passed through a high efficiency particulate air filter (HEPA) where the particulates are collected and the gas is released.

Carbon dioxide snow is formed when liquid CO₂, which is allowed to expand to atmospheric pressure through a nozzle, forms soft flakes. CO₂ snow technology can remove particles and debris without damage to the surface. It is effective for dust and dirt but not necessarily grease unless the pressure is between 400-800 psi.



Chemistries and Equipment?

CO₂ pellet technology compresses CO₂ snow into hard pellets that are blasted toward a surface with a high pressure carrier gas, typically compressed air. The pellet process can remove paint and rust but there is a greater risk of harming the surface than with CO₂ snow. Pellets are effective at removing oil and grease at relatively low pressures. These CO₂ techniques have been used for precision cleaning applications in the aerospace and electronics industries for many years. Fragmented CO₂ is a relatively new technology where the CO₂ solid particles are randomly shaped, unlike pelletized CO₂, which has uniform shape. Fragmented CO₂ requires less equipment resulting in lower capital cost. It is also effective at removing oils and greases at relatively low pressures.

Supercritical Carbon Dioxide

Supercritical fluids (SCFs), which result from subjecting substances to temperatures and pressures above their critical points, possess properties intermediate between liquids and gases. Precision surface cleaning with SCFs takes advantage of these unique properties, such as liquid-like density and solvency combined with gas-like viscosity and diffusivity. SCFs can rapidly penetrate substrates and small interstitial spaces, dissolve the contaminants, and then be easily and completely removed since the SCF lacks surface tension.

SCF cleaning is typically a batch process performed using a system consisting of two primary pressure vessels (a cleaning chamber and a separator), high pressure pumps, pressure regulators, pressure reduction valves, and interconnecting piping. The cleaning process itself may involve simple immersion of the parts in the SCF for a given time period, or may incorporate SCF agitation and recirculation, and/or displacement of the contaminated SCF with fresh SCF. Recovery and reuse of the CO₂ may be economically justified depending on the process scale.

Media Blasting

The media blasting process, in general, combines an abrasive media, a pressurized delivery system and one of a variety of cleaning chambers. Typically called impact or abrasive cleaning, this method of cleaning leaves no residue. Abrasive cleaning is not typically appropriate for grossly

contaminated parts because the contaminants can cause the media to stick together. However, media cleaning is appropriate for ordinary machining oils and contaminants. Glass beads and sand have been used as media in this process for years with the more recent introductions of plastic, sodium bicarbonate and wheat starch. These newer media allow the technology to be used on a wider variety of substrates.

Solvent Cleaning

Solvents in 100% concentration are used in a variety of cleaning applications. Some have been used for many years, such as the non-chlorinated solvents (e.g., acetone, alcohols, ketones) and the petroleum distillates (e.g., mineral spirits, Stoddard solvents and naphtha solvents). Low vapor pressure solvents such as terpenes, esters, glycols, ethers and N-methyl pyrrolidone are used in certain applications. Hydrochlorofluorocarbons (HCFCs) were developed as temporary replacements for CFCs; however, HCFCs do contribute to the depletion of the ozone layer. (For more information, see TURI's SCL Fact Sheet #2). Many non-chlorinated, fluorinated solvents have also been developed recently such as hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) and perfluoroethers (PFEs).

For non-flammable solvents, a common method of solvent cleaning is vapor degreasing. A vapor degreaser is a tank with heating coils in the bottom and a condensing zone near the top. The solvent temperature is raised to near boiling and the hot solvent vapor fills the tank up to the condensing zone. The vapor condenses on the dirty workpiece dissolving the contaminants and drains back into the solvent reservoir. Solvent losses occur mainly when the vapor zone is disturbed by air drafts, when the workload is lowered into or raised out of the machine, or when the parts drag out condensed solvent. Recent developments in cleaning equipment now offer "closed" systems for solvent cleaning to minimize releases.

No single solvent has provided the perfect cleaning solution for all applications. Among the many things to consider when choosing a solvent for cleaning are the potential environmental, health and safety impacts, solvency, flammability, stability, cost, whether it is regulated as a VOC and whether it has been approved federally as a SNAP (Significant New Alternative Policy) cleaning alternative.



Where can Additional Information be Found?

Free, on-site technical assistance is available for Mass. companies from the Office of Technical Assistance for Toxics Use Reduction at 617-727-3260.

TURI

Toxics Use Reduction Institute, "The Cost of Changing: Total Cost Assessment of Solvent Alternatives," University of Massachusetts Lowell, 1994.
Toxics Use Reduction Institute, EPA Draft Report, "Evaluation of Alternatives to Chlorinated Solvents for Metal Cleaning," September 1996.
Toxics Use Reduction Institute, "Closed Loop Aqueous Cleaning," Technical Report No. 29, September 1995.
Toxics Use Reduction Institute, Surface Cleaning Laboratory Case Studies #1-3, 1995.
Toxics Use Reduction Institute, Surface Cleaning Series Fact Sheet #2, "HCFCs," 1996 and Fact Sheet #3, "The Drying Options," 1997.

U. S. Environmental Protection Agency

USEPA, Office of Air and Radiation, "Alternatives for CFC-113 and Methyl Chloroform in Metal Cleaning," June 1991.
USEPA, Office of Research and Development, "Guide to Cleaner Technologies: Alternatives to Chlorinated Solvents for Cleaning and Degreasing," EPA/625/R-93/016, February 1994.
USEPA, Office of Research and Development, "Guide to Cleaner Technologies: Cleaning and Degreasing Process Changes," EPA/625/R-93/017, February 1994.
USEPA, Office of Research and Development, "Demonstration of Alternative Cleaning Systems," EPA/600/R-95/120, August 1995.
USEPA, Office of Solid Waste and Emergency Response, "Waste Minimization in Metal Parts Cleaning," EPA/530-SW-89-049, August 1989.
The EPA offers a computer-assisted guide for solvent alternatives known as SAGE. SAGE is available through the Control Technology Center of the EPA Air and Energy Engineering Research Laboratory. To receive a disk copy, contact the hotline at 919-541-0800.

Additional Articles and Publications

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Kranz, P.B., Erie County of Environment and Planning, Division of Environmental Compliance, "Ultrasonic Cleaning as a Replacement for a Chlorofluorocarbon-Based System", Buffalo, New York, November 1993.
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US Army Corps of Engineers, Construction Engineering Research Laboratories, Technology for Waste Solvent/Oil Recycling, "Aqueous Alkaline Cleaners: An Alternative to Organic Solvents," September 1993.
US Department of Energy & US Air Force, "Solvent Substitution for Pollution Prevention," Noyes Data Corporation, Park Ridge, NJ, 1993.
Wolf, Katy, "The Generic Classification System: A Simplified Approach to Selecting Alternatives to Chlorinated Solvents," *Pollution Prevention Review*, Winter 1993-94, pp. 15-29.

Periodicals

Precision Cleaning, P.O. Box 3329, Lowell, MA 01853-9975
Microcontamination - Ultraclean Manufacturing Technology and Management, P.O. Box 21651, St. Paul, MN 55121
Plating and Surface Finishing - Journal of the American Electroplating and Surface Finishing Society, Inc., 12644 Research Parkway, Orlando, FL 32826

Conferences

Precision Cleaning (annual)
Mr. Clean (semiannual)
International CFC and Halon Alternatives (annual)
AESF/EPA Pollution Prevention and Control (annual)
International Workshop on Solvent Substitution (annual)

Web Sites

TURI's Surface Cleaning Laboratory <http://www.cleaning.org>
Research Triangle Institute <http://www.clean.rti.org>
EPA <http://www.epa.gov>





HCFCs & Cleaning

What are HCFCs?

HCFCs, or hydrochlorofluorocarbons, are similar to chlorinated fluorocarbons (CFCs) except that some of the chlorine molecules are substituted with hydrogen. Touted as replacements for CFC solvents, the addition of hydrogen molecules reduces but does not eliminate the compounds' ozone depletion potential (ODP). Prompted by the Montreal Protocol, the US Environmental Protection Agency (EPA) adopted a phaseout program for all ozone depleting substances (ODSs) in Title VI of the Clean Air Act Amendments (CAAA) of 1990.

Other potential CFC alternatives such as hydrofluorocarbons (HFCs) contain no chlorine but their often high vapor pressure and low solubility make them poor cleaners, with the possible exception of HFC-4310. While some halogenated compounds containing fluorine or bromine (e.g., perfluorocarbons or dibromomethane) do exhibit good cleaning properties, they also have damaging environmental and toxicological effects.

How Is CFC & HCFC Use Restricted?

Section 602 of the CAAA created two classes of ODSs. The Class I list of chemicals contains all fully halogenated CFCs, fire-retardant halons, HCFC-precursor carbon tetrachloride (tetrachloromethane) and methyl chloroform. In general, Class I chemicals possess an ODP of 0.2 or greater. All groups in this class reached their production phaseout date on January 1, 1996.

The Class II list of chemicals contains the HCFCs. Section 605 of the CAAA set accelerated phaseout dates for three HCFCs with relatively high ODPs: HCFC-22, HCFC-141b and HCFC-142b. For cleaning applications, production and importation of HCFC-142b and HCFC-22 will be banned in 2010 and the remaining HCFCs in 2015. As with some of the CFCs, the phaseout schedule for HCFCs may be further accelerated with the development of more and effective non-ozone depleting alternatives.

ODS replacements are also restricted by the EPA Significant New Alternatives Policy (SNAP). SNAP lists acceptable and unacceptable substitutes for specific uses.

For example, HCFC-141b is unacceptable for cleaning as of January 1, 1996. The SNAP list is updated periodically in the US Federal Register.

CFCs and HCFCs also contribute to global warming. The Clean Air Act (CAA) lists the global warming potential (GWP) and atmospheric lifetimes of several chemicals. These values can be used to determine the environmental consequences associated with different halogenated solvents. For instance, hydrofluoroether (HFE), recently listed by the EPA as a substitute only for Class I substances methyl chloroform and CFC-113 in metal, electronic and precision cleaning has a GWP of 150-480 and an atmospheric lifetime of 4.1 years.

Are All HCFCs Used for Cleaning?

No. Most are typically used in foam-blowing or as refrigerants. Many HCFCs used for solvent cleaning are blends or azeotropic mixtures with alcohols and/or ethers. The ODPs and GWPs of these mixtures can be determined by taking the individual characteristics for each chemical, multiplying by their respective weight fractions and summing them together.

For more information, please contact:

- EPA's Stratospheric Ozone Information Hotline at 1-800-296-1996 or Internet <http://www.epa.gov/>
- TURI's Technology Transfer Center (TTC) at (508) 934-3346 or Internet <http://www.turi.org/~turi/>
- TURI's Surface Cleaning Laboratory (SCL) at (508) 934-3249 or Internet <http://www.cleaning.org>

• The Toxics Use Reduction Institute (TURI) is a multi-disciplinary research, education and policy center established by the Massachusetts Toxics Use Reduction Act (TURA) of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce.

Please turn page.

Summary of Related HCFC/CFC Environmental Data

Chemical Name	Formula <mol. weight>	Synonyms	CAS # Chem. Abstract	Cleaning Phaseout Dates ¹	ODP (CFC 11 = 1)	GWP ⁶ (CO ₂ = 1)	Exposure Limit (parts per million)	Atmospheric Lifetime
Chlorodifluoro- methane	CHClF ₂ <86.47>	HCFC-22 Freon 22	75-45-6	2010 ²	0.05	1700	1000 PPM	15.3 years
2,2-Dichloro- 1,1,1-trifluoro- ethane	C ₂ HCl ₂ F ₃ <152.93>	HCFC-123 Freon 123	306-83-2	2015 ²	0.02	93	AEL 30 PPM (Average Exposure Limitation)	1.6 years
2-Chloro-1,1,1,2- tetrafluoroethane	C ₂ HClF ₄ <136.48>	HCFC-124 Freon 124	2837-89-0	2015 ²	0.02	480	500 PPM	6.6 years
1,1-Dichloro- 1-fluoroethane	C ₂ H ₃ Cl ₂ F <116.95>	HCFC-141b Freon 141b	1717-00-6	1996 ^{2,3} (1997 ⁴)	0.12	630	500 PPM	7.8 years
1-Chloro-1,1- difluoroethane	C ₂ H ₃ ClF ₂ <100.50>	HCFC-142b Freon 142b	75-68-3	2010 ²	0.06	2000	1000 PPM	19.1 years
3,3-Dichloro- 1,1,1,2,2- and 1,1,2,2,3- penta- fluoropropane	C ₃ HCl ₂ F ₃ <202.94>	HCFC-225ca and HCFC-225cb isomeric blend	422-56-0 ca 507-55-1 cb	2015 ^{2,5}	0.03 ca 0.03 cb	170 ca 530 cb	Company set at 25 PPM / ca Manufacturer set at 50 PPM / blend	1.6 years ca 5.1 years cb
1,1,2-Trichloro- 1,2,2-trifluoro- ethane	C ₂ Cl ₃ F ₃ <187.38>	CFC-113	76-13-1	January 1, 1996	0.80	5000	1000 PPM	90 years
1,1,1-Trichloro- ethane (TCA)	C ₂ H ₃ Cl ₃ <133.42>	Methyl (MCF) chloroform	71-55-6	January 1, 1996	0.10	110	350 PPM	6.3 years

1 - Chemical cannot be produced or imported for cleaning usage after the phaseout date; inventoried or recycled stock available for use.

2 - Phaseout schedules for refrigeration and feedstock uses are different (CAAA Sections 601-607).

3 - Use restricted by EPA SNAP (CAA Significant New Alternatives Policy) list.

4 - Proposed extension by EPA SNAP for existing users in precision cleaning and high performance electronics only.

5- HCFC-225ca isomer used for electronics and precision cleaning; HCFC-225 isomeric blend not approved for metal cleaning.

6 - Based on 100-year horizon.



Alternatives to Petroleum- and Solvent-Based Inks

Substitute inks available for lithographic, flexographic, and gravure printing can reduce concerns associated with the use of conventional petroleum-based lithographic inks and solvent-based flexographic and gravure inks. This fact sheet summarizes these substitution alternatives. It describes the composition of substitute inks and some use considerations and includes an alternatives matrix that provides comparative information on each alternative, including operational, cost, and quality considerations. Articles, guides, and industry case studies are also listed.

Although inks are not always considered the major source of VOCs and solvents in the printing industry, the decision to use substitute inks can be a beneficial part of an overall toxics use reduction program and can help reduce the use of hazardous or toxic substances in other materials such as cleaning solutions.

Ink substitutions include:

- Vegetable oil inks
- Radiation-curable inks
- Water-based inks

The substitution alternatives presented in this fact sheet are not all-inclusive, nor is one ink substitute recommended over another. Examination of substitute inks should involve thorough consideration of environmental and health and safety tradeoffs at all stages of printing, including raw materials acquisition, processing, and recycling or disposal, and any new or unknown hazards in the alternative materials.

Alternative Ink Materials

Vegetable oil inks contain vegetable oils as a replacement for some or all of the petroleum oil in lithographic inks. They are available for heatset and non-heatset web presses and for sheetfed presses and generally require no equipment changes. While various compositions of oils such as linseed, soy, and tung may be used, many vegetable inks today are soy-based. Because vegetable inks penetrate paper more slowly and set primarily by oxidation, they generally have longer drying times. Most vegetable inks contain some petroleum oil to hasten drying or setting time to acceptable standards. The amount of vegetable oil replacing the petroleum oil varies with the manufacturer and also depends on:

Press type — for example, heatset inks require more petroleum oil than non-heatset inks.

Paper type — with more absorbent paper a higher percentage of vegetable oil may be used.

Ink color — black soy-based inks dry more slowly than color soy-based inks.

Because soy oil is clearer than petroleum or linseed oils, soy ink may provide better print quality and brighter colors. The American Soybean Association (ASA) has set standards for the percentage of soy oil in inks and permits use of its "SoySeal" for those that meet minimum requirements for soy oil content, depending on ink type. Although some new color soy inks contain non-toxic pigments and other additives, soy or other vegetable inks may contain hazardous or toxic materials in the pigments, drying compounds, and additives.

Radiation-curable inks include **ultraviolet ink** and **electron beam ink**. They consist of one or more monomers and oligomers that polymerize on exposure to radiation. They generally contain no solvent and are particularly recommended for some applications in lithography and letterpress.

Water-based inks are usually composed of pigmented suspensions in water and film formers. Their best application is in flexographic printing on paper, but they are also recommended for some types of gravure printing. Both low-solvent and 100% water-based inks are available.

Substitute Inks by Type

Heatset Inks

Use of vegetable-based heatset inks provides some reduction in VOCs compared with conventional heatset inks. Because heatset printing relies on evaporation and vegetable inks dry primarily by oxidation, substitute heatset inks usually contain a higher level of VOCs than do substitute inks for non-heatset or sheetfed presses. Vegetable oil heatset inks commonly contain 30-35% petroleum oils by weight. Increasing the vegetable oil content increases dryer temperature requirements and can cause scorching of paper and dulling of finished ink film. The dryer heat also volatilizes the ink oils, generating VOC emissions. Ink cost can be 5-8% higher. Soy heatset inks receiving the ASA SoySeal must contain a minimum of 7% soy oil by weight.





Non-Heatset Inks

Vegetable oil inks can be used for both non-heatset web and sheetfed presses and can contain a higher vegetable oil content than heatset inks. They can provide better print quality and brighter colors. Soy-based color inks have a lower overall oil content than soy-based black inks, and therefore dry faster. A higher percentage of the oil in color inks can be soy-derived. Printing on uncoated paper also permits a higher vegetable oil content than printing on coated paper. Ink cost is often higher than that of conventional inks, but is expected to decrease. Non-heatset inks receiving the ASA SoySeal must contain a minimum of 30% soy oil (web inks) or 20% soy oil (sheetfed inks).

Newsprint Inks

Newsprint inks can contain a high vegetable oil content due to the absorbency of newspaper. Because the ink dries solely by absorption, it is possible to substitute all of the petroleum oil with vegetable oil, and 100% soy formulations are available. For color newsprinting, soy inks provide brighter colors, better color control, and less rub-off. Soy inks are less likely to build up on the plate, have less tendency to skin over, and greater stability. They permit greater latitude in ink-water balance, allowing more flexibility in press settings, and provide greater coverage per pound of ink. Although black soy-based ink can cost up to 30% more than conventional ink, the higher cost may be offset by greater coverage and reduced newsprint spoilage due to its smoother flow. Newsprint inks must have a minimum soy content of 40% (black ink) and 30% (color ink) to receive the ASA SoySeal.

Form Inks

The absorbency of forms paper permits a fairly high vegetable oil content in form ink. Vegetable oil form inks provide brighter colors than conventional inks. To receive the ASA SoySeal, form inks must contain at least 20% soy oil by weight.

Radiation-Curable Inks

Ultraviolet (UV) and electron beam (EB) inks cure by polymerization on exposure to UV or EB energy. Because they contain no solvents, they release no VOCs. They can be used on both web and sheetfed presses. Because the inks do

not dry on the press, they can remain in ink fountains for long periods and reduce press cleaning frequency. Main disadvantages are the high cost of capital equipment and the potential for worker exposure to UV or EB light, which necessitates shielding and other safety devices built into the equipment. Radiation-curable inks may contain toxic chemicals, and prolonged contact can cause dermatitis and skin sensitivity. The cost of UV ink can be twice that of conventional solvent-based inks; EB ink cost is also higher, although less than UV ink. Paper printed with radiation-curable inks cannot be de-inked by conventional means.

Flexographic and Gravure Inks

The use of water-based inks in flexographic and gravure printing can reduce worker health and safety risks, air pollution control requirements, and liability and waste disposal costs associated with the use of alcohol solvents. Water-based inks permit replacement of solvent-based cleaners with non-VOC-containing substitutes. They hold their color and viscosity for longer periods during print runs and may provide better print quality. Because these inks cannot be cleaned with water when dried, equipment must be cleaned more frequently. Water-based inks are less forgiving of imperfec-

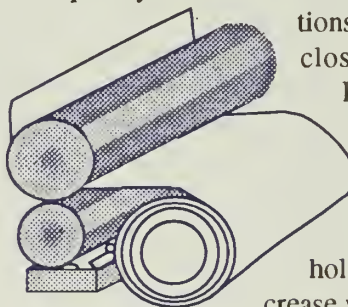
tions in equipment and may require closer monitoring of operations.

Equipment and process modifications may be necessary. Currently, even inks labeled 100% water-based may contain low levels of solvent, usually alcohol, to enhance adhesion and increase wetting. In some cases, pretreat-

ment may be required before discharging

water-based inks to POTWs. Some water-based inks may still contain heavy metal pigments that must be disposed of as hazardous waste. De-inking of material printed with water-based inks may be difficult.

A new water-washable ink with a "solubility conversion mechanism" has been formulated for lithographic printing. This vegetable-oil-based ink acts as a conventional insoluble lithographic ink during printing but can be converted to a soluble state and removed from press equipment with a simple water solution. The ink can be used with conventional equipment.



SUMMARY OF PRODUCT SUBSTITUTION ALTERNATIVES TO PETROLEUM- AND SOLVENT-BASED INKS

Alternative	Applications	Toxics Use Reduction Benefits	Operational Advantages	Operational Disadvantages	Cost	Product Quality	Limitations
Vegetable Oil Heatset Inks	Lithographic web presses	Reduced VOC emissions and worker exposure to petroleum oils		Slower drying time; poor drying can result in set-off, marking, and poor rub resistance	No capital cost; ink cost can be 5-8% higher	Similar quality	Heatset requirements limit replacement of petroleum oils; ink dryer contributes to VOC emissions; ink waste may still be hazardous
Vegetable Oil Non-heatset Inks	Lithographic non-heatset web and sheet-fed presses	Reduced VOC emissions and worker exposure to petroleum oils	Can provide better print quality, brighter colors, better pickup and transfer	Slower drying time	No capital cost; ink cost slightly higher	Similar quality, brighter colors and improved clarity	Usually contain some petroleum oils; ink waste may still be hazardous
Vegetable Oil Newsprint Inks	Lithographic web presses	Reduced VOC emissions and worker exposure to petroleum oils; 100% replacement of petroleum oils possible	Better color reproduction; better color control; less rub-off; less tendency to build up or skin over; greater stability; smoother flow; better coverage; greater ink-water balance parameters permit more latitude in press settings	Usually slower drying time	No capital cost; higher ink cost may be offset by reduced newsprint spoilage	Higher quality color printing; similar quality black printing	May contain some petroleum oils; ink waste may still be hazardous
Vegetable Oil Form Inks	Lithographic non-heatset web presses	Reduced VOC emissions and worker exposure to petroleum oils	Smother flow, better coverage	Slower drying time	Slightly higher ink cost	Higher quality color printing	May contain some petroleum oils; ink waste may still be hazardous
UV Curable Inks	Lithographic web and sheet-fed presses	No ink-derived VOC emissions or worker exposure to petroleum oil; reduced process waste	No ink drying on press reduces frequency of press cleaning; rapid curing; no set-off; no need for ventilation of printed sheets		Capital equipment cost; higher ink cost; lower energy use than thermal drying; increased productivity	Good gloss and durability; print quality may be less clear; possible adhesion problems on some materials (aluminum, steel, some plastic)	Workers must be protected from UV light; some toxic chemicals in inks; may cause skin sensitivity; ventilation needed to reduce ozone buildup; paper difficult to recycle
EB Curable Inks	Lithographic web and sheet-fed presses	No ink-derived VOC emissions or worker exposure to petroleum oil	No ink drying on press reduces frequency of press cleaning; rapid curing; no set-off; no need for ventilation of printed sheets		Capital equipment cost; considerably higher ink cost	Print quality less clear	Workers must be protected from EB light; some toxic chemicals in inks; may cause skin sensitivity; often degrade paper; paper difficult to recycle
Water-based Inks	Flexographic and gravure presses	Little or no ink-derived VOC emissions or worker exposure to alcohol; allow replacement of solvent-based cleaners and fountain solutions with safer substitutes	Hold color and viscosity longer during press runs; more coverage per pound of ink; reduce need for make-up solvent during printing	Require more frequent equipment cleaning; less forgiving of equipment imperfections; may cause paper curl	May require new capital equipment, greater energy use; reduced hazardous waste disposal and liability costs	Similar quality with new equipment; low ink gloss on porous substrates	May contain low level of solvent; ink waste may still be hazardous; greater energy use for drying



References

Resources listed are available from the publisher and may be viewed at the Technology Transfer Center of the Massachusetts Toxics Use Reduction Institute. To order U.S. EPA publications, call EPA's Pollution Prevention Information Clearinghouse: 703-821-4800. Information for contacting other publishers is available from the Institute.

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- "Substitution Case Study: Alternatives to Solvent and Petroleum-Based Inks." Technical Report No. 5. Lowell, MA: Massachusetts Toxics Use Reduction Institute, May 1993.
- "Toxics Use Reduction Success Story. Deluxe's Solvent-Free Printing System" (Fact sheet). Boston: Office of Technical Assistance, Massachusetts Executive Office of Environmental Affairs, 1994.
- "Vegetable Inks Make the Grade." *In Business*, September/October 1992.

Industry Case Studies

The following case studies were produced by the U.S. EPA, Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, OH.

- Miller, Gary D., William J. Tancig, Michael J. Plewa, and Paul M. Randall. "Ink and Cleaner Waste Reduction Evaluation for Flexographic Printers." (Project Summary). July 1993. EPA/600/SR-93/086.
- Process Modification and Product Substitution for VOC Emission Reduction in the Flexographic Printing Industry. Amko Plastics, Inc." In Tillman, Joseph W., *Achievements in Source Reduction and Recycling for Ten Industries in the United States*. September 1991. EPA/600/2-91/051.
- Reduction of VOC Emissions via Product Substitution and Recycling of Solid Waste in the Commercial Sheet-Fed Printing Industry. Terry Printing, Inc., Janesville, Wisconsin." In Tillman, Joseph W. *Achievements in Source Reduction and Recycling for Ten Industries in the United States*. September 1991. EPA/600/2-91/051.

Additional case studies:

- "Kemp Furniture Industries, Inc., Print Division: Material Changes Can Reduce Hazardous Waste Generation" (Abstract). Raleigh, NC: North Carolina Pollution Prevention Pays Program.
- "Product Labels: Company Has Reduced Waste Generation from Label Printing Operations" (Abstract). Raleigh, NC: North Carolina Pollution Prevention Pays Program.

Technical information in this fact sheet was drawn in part from Technical Report No. 5, "Substitution Case Study: Alternatives to Solvent- and Petroleum-Based Inks," prepared for the Toxics Use Reduction Institute by Tellus Institute. Technical guidance was also provided by George Frantz, Office of Technical Assistance, Massachusetts Executive Office of Environmental Affairs, Gary Jones, Graphic Arts Technical Foundation, Pittsburgh, PA, and Paul Volpe, National Association of Printing Ink Manufacturers, Hasbrouck Heights, NJ.

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce.





Process Control for Surface Finishing

"Process control" and "quality control" have undergone drastic changes in the United States over the past two decades. Under international quality programs (e.g., ISO 9000) and internal corporate quality programs, the emphasis has moved from in-process and final product quality testing to a process-oriented system. This process-oriented control system provides that the process is operated in a consistent, reproducible and accurate manner.

When process problems arise, they can be evaluated using a system where performance criteria are well documented and discrepancies are easier to identify. If a problem is pervasive and systematic, some improvement can be implemented in a logical manner with identifiable goals and a well-defined strategy.

The surface finishing industry has many individual processes that encompass the universe of operations. These processes operate most efficiently within certain parameters. When these parameters are not met, the result is most often poor quality of the final finish. Without a reliable process control system, the finisher may not be able to determine the root cause of the quality problem, and will likely waste money by wasting materials and processing time. This fact sheet discusses the specific importance of a process control system in surface finishing operations and provides the basic elements of such a system.

Importance of a Process Control System

A properly designed and implemented process control system is important to the finisher for the following reasons.

- Facilitates timely identification of the causes of finishing problems, avoiding costly attempts to fix an undiagnosed problem.
- Aids in reducing rejected or off-specification parts, resulting in substantial savings to the finisher. When parts are rejected, it more than simply doubles materials use. The parts must be stripped in a chemical solution and the resulting waste must be treated on-site or shipped off-site as hazardous waste. Also, labor costs, quality resources, administrative resources and management resources will be increased due to rejected parts
- Enhances the reputation of the finishing shop as a quality-driven, quality-conscious shop that has lower operating costs, better environmental performance, and better quality.

Example

Problem: non-adherent plating on parts

Attempted Solution with no Process Control Program: dispose of the entire cleaning line

Diagnosis using a Process Control Program: pickling solution has been depleted of acid below the lower control limit

Alternate Solution: add acid to pickling bath



Elements of a Process Control System

A properly designed and implemented process control system requires the following basic steps.

- Identify appropriate parameters to be tested such as solution components and contaminants
- Identify proper test methods
- Establish upper and lower control limits for the parameters based on vendor information, literature and experience
- Establish adequate testing frequency
- Install a chemical maintenance routine for chemical additions and solution purification, decants or solution changes

Identification of Appropriate Parameters

Identification of the appropriate parameters to test is the first step to a successful process control program. It is important to test both the components that were purposely added (solution components) and those that were not (contaminants).

Solution Components

While no "typical" metal finishing solutions exist, the major components of a plating bath can be divided into two categories, inorganic (e.g., the metal to be plated, the acid or alkaline matrix, additional salts if required) and organic (brighteners and grain refinishers).

For most inorganic components, the finisher can easily determine the chemical concentration by performing wet chemical titrations.

Because the direct analysis of organic components requires expensive equipment and highly trained operators, these components are rarely measured directly. Generally, they are measured indirectly by plating solution performance. Vendors may provide direct analysis on request.

Contaminants

Contaminant analysis is as important as the analysis of solution components because their presence can result in poor quality work, expensive down-time during post-failure analysis, and potential customer dissatisfaction. Contaminants can be divided into the following groups based on their origin.

- Materials dragged in from upstream processes (e.g., oils from cleaning baths or metals from acid pickles)

The Hull Cell Test

The classic Hull-Cell test allows the finisher to test the effects of modifying the process parameters in a small volume cell. By modifying the chemistry and/or the physical parameters, improvements in the process can be made.

In the Hull-Cell test, a small volume of solution (less than 1/2 liter) is plated using a small rectifier and specially designed plating cell. Parameters such as current density, temperature, agitation, and inorganic and organic component concentrations can be modified.

For example, by making small additions of organic additives and observing the quality of the plate after modification, the correct addition quantities can be determined for the full-scale bath.



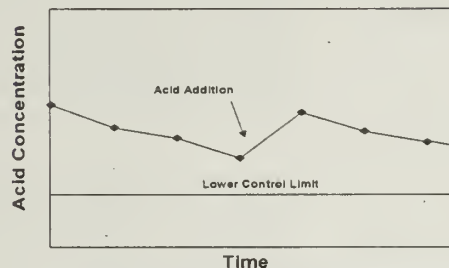
- Impurities in the components that are added to the solution
- Break-down products of the components (e.g., heat and electrical current will degrade organic additives, such as brighteners, inhibiting their effectiveness)
- Chemicals added from incoming water or atmospheric absorption (e.g., carbonate build-up from atmospheric carbon dioxide)

Due to their low concentration and chemical nature, contaminants are generally tested by trained operators using expensive equipment. Contaminant testing services are often offered by chemical vendors or can be contracted to a testing laboratory. In both cases it is important to review potential contamination sources and their potential negative effects with the tester. A schedule must be determined for this testing, including a system for sampling, transportation, analysis and documentation.

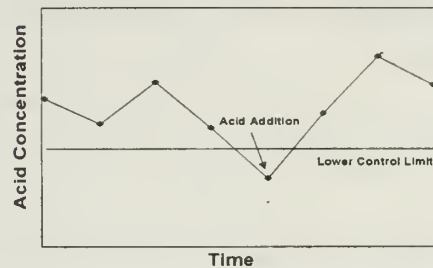
Proper Test Methods

For proprietary solutions, vendors provide the appropriate test methods. For common solutions, test methods are available from commercial texts, metal finishing journals and general chemical references.

For good process control, the time between testing and additions must not allow chemical concentration to fall below lower control limits.



With poor process control, wide swings in parameters result, potentially causing poor product quality.



Upper and Lower Control Limits

Upper and lower control limits are generally provided by the vendor of the process, or are available from the standard literature in the case of non-proprietary processes. Statistical process control (SPC) methods can be used to determine upper and lower control limits in an SPC environment. Specific texts or SPC guides should be consulted for more detailed information.

Testing Frequency

Testing must be performed on a schedule that assures that chemical concentrations will not drop below the lower allowable limit. In some cases, tests should be performed on a per-shift basis. In other cases, testing may be performed weekly. Contaminant testing may be done less frequently.

The time period between tests on both solution components and contaminants depends on the following factors.



Production Rate

The greater the production rate, the greater the amount of dragout and consumption.

Upstream Rinsing

Generally, efficient upstream rinsing will cause less contamination of the process solution. For example, when acid processes and alkaline processes are side by side, efficient rinsing ensures that less neutralization (chemical loss) will occur.

Nature of the Solution

In many plating solutions, metal concentration must be checked only once or twice per week, regardless of production rate. This is because the solution uses metal anodes that slowly dissolve into the solution, replacing plated or lost metal ions. However, the acid or alkaline matrix must be checked several times per week due to dragout and/or consumption.

Chemical Maintenance

Chemical Additions

After analysis has been performed, the chemist or finisher calculates the total chemical add that must be made to correct the concentration. This is a crucial step; following are a few tips to ensure that it is done correctly.

- Double-check the calculations to be sure they are correct.
- Be sure that the calculations use the working tank volume and that the solution in the tank is at the correct working level.
- If dragout solution or water must be added to correct the tank volume, allow the solution to mix thoroughly prior to sampling.

Avoiding Chemical Loss

Dragout

Solution is entrained on the surface of the parts, racks or barrels and "dragged-out" of the processing tank and into the subsequent rinse tank

- remove the workpiece at a slower rate
- increase drip time
- install drain boards or drip bars between baths
- maintain racking designs that achieve maximum draining
- install air knives or spray or fog rinses above process tanks

Consumption

Dragout of the alkaline cleaner into the acid pickle will result in neutralization (destruction) of the acid. In cyanide plating, cyanide is oxidized when current is applied.

- consumption caused by neutralization via drag in of chemicals can be reduced by good dragout and rinse procedures
- consumption caused by electrolytic destruction of organics is very difficult to avoid

Air Emissions

These losses are generally much lower than dragout and consumption, except in the case of vapor degreasing.

- switch to a non-volatile cleaning process
- increase freeboard on process tanks
- add foam blankets, floating polypropylene balls or automatic covers to tanks
- install scrubbers, demisters or condensate traps on ventilation or exhaust systems
- if segregated, some scrubber waste can be reused in the process bath
- do not operate the process bath above the desired temperature



- Adds must be performed soon after analysis so that the concentration does not fall below the lower limit.

Feed and Bleed

The "Feed and Bleed" method of chemical additions uses an automatic sensor (simple level control, density control, or chemical sensor) to determine the need for additions. The solution is automatically pumped into the tank (feed), and a corresponding amount drains out of the tank (bleed) via gravity into waste treatment or waste storage. This method is excellent for process control, but causes additional waste, because the chemistry has not completely reacted. A study of the trade-off between chemical and waste treatment costs and efficiency improvements must be made to determine if "feed and bleed" is an appropriate control method.

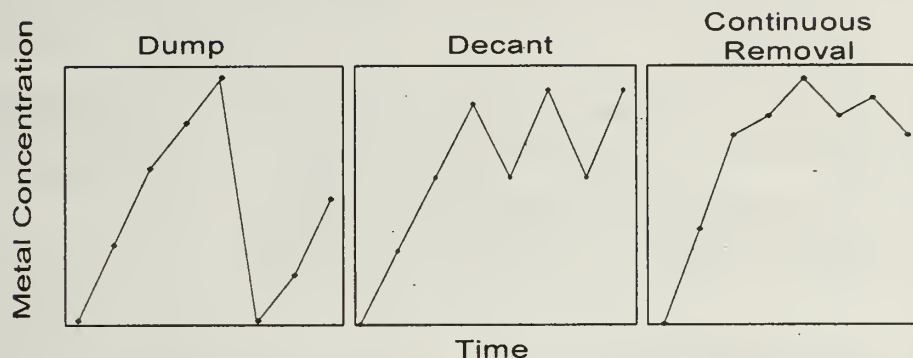
Solution Purification, Decants and Solution Changes

Plating solutions are purified by two methods: carbon filtration for organic removal and low current density plate out (dummying) for metallic contaminant removal.

Solutions that tend to remove materials (e.g., alkaline cleaning solutions that remove oils and dirt from the surface of parts, or anodizing solutions that remove aluminum) traditionally have been purified by complete dumping and replacement, or by decanting, which is the removal of a certain volume and replacement of that volume.

The process control goals for chemical solutions are

Pickling Solution Metal Concentrations
for Three Control Methods



to keep the contaminant concentration both constant and at some appropriate limit. The economic goal is to achieve the process control goals at the lowest cost (i.e., least raw materials, least waste, least labor). From a process control standpoint, the dumping and replacement method does not achieve either goal. The decant method of solution control keeps the processing conditions more constant than the dump method, but increases chemical use because solutions have not been used up to maximum allowable contamination. This increased use of chemicals increases the cost of raw materials, waste disposal and labor.

Luckily technology has come to the rescue to help solve this process control vs. chemical use conundrum. Innovative methods are being developed that decrease chemical use while improving process control:

- Ultrafilters that continuously remove oil and dirt from alkaline cleaning solutions
- Diffusion Dialysis units that remove metals from pickling, desmutting, anodizing and stripping solutions
- Acid Sorption units that remove metals from anodizing baths



The economics, level of technical expertise required, and other issues need to be determined on a case by case basis using total cost assessment principles including an understanding of potential regulatory benefits and issues, potential liability issues and the potential for corporate enhancement.

Conclusion

In today's quality conscious manufacturing environment, a surface finishing facility can improve its operations by implementing a process control program. By operating the program in a consistent manner and understanding the critical processing criteria, continuous improvement can be a reality.

Useful Information

Books

"Industrial Ventilation, A Manual of Recommended Practice," American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, BLDG. D-7, Cincinnati, OH 45211. This manual covers appropriate ventilation for metal finishing operations and includes tables on emissions from various operations.
<http://www.acgih.org/>
<http://www.ccohs.ca/products/acgih/industrialventilation.html>

"Industrial Wastewater Treatment Technology," Patterson, James, Butterworth Publishers, 80 Montvale Avenue, Stoneham, MA 02180. This text covers pollution control topics of interest to the electroplater. Of primary interest, from a toxics use reduction standpoint, are the economic analyses presented on treatment cost.

"Metal Finishing Guidebook and Directory," 660 White Plains Road, Tarrytown, NY 10591-5153. Published yearly by Metal and Plastics Publications, Inc. as a thirteenth issue to the monthly Metal Finishing Magazine. General guide to all phases of electroplating and metal finishing, including ancillary topics such as waste treatment and rinsing.

"Modern Electroplating," Lowenheim, Frederick, John Wiley & Sons, Wiley-Interscience Publications. A relevant text that covers electroplating processes in intimate chemical detail.

"Pollution Prevention and Control Technology for Plating Operations," Cushnie, George, Jr., National Center for Manufacturing Sciences, 3025 Boardwalk Drive, Ann Arbor, MI 48108-3266. A compilation of pollution prevention options for plating operations, including a useful survey/database.
<http://www.nmfrc.org/>

"Water and Waste Control for the Plating Shop," Kushner, Arthur and Kushner, Joseph; Gardner Publications, 1994. This is the essential text on rinsing. In an orderly progression, shows mathematically how to achieve proper rinsing while minimizing water use.
<http://www.hansergardner.com>

Journals and Publications

"Guides to Pollution Prevention: Metal Finishing Industry," U.S. Environmental Protection Agency, October 1992, EPA/652/R-92-011.
<http://www.epa.gov/ncepihom/Catalog/EPA625R92011.html>

Plating and Surface Finishing, the Journal of the American Electroplating and Surface Finishing Society, 12644 Research Parkway, Orlando FL 32826-3298. Advanced articles on plating processes and departmentalized columns on regulatory, pollution prevention, and process issues.
<http://www.aesf.org/>
<http://www.aesf.org/psf.htm>

Precision Cleaning, Witter Publishing Co., Inc., 84 Park Avenue, Flemington NJ 08822. This magazine is devoted to cleaning issues, including solvent replacement and aqueous cleaning.
<http://www.precisioncleaningweb.com>

Products Finishing, 6600 Clough Pike, Cincinnati, OH 45244-4090. A useful magazine covering many aspects of metal finishing, including process and pollution prevention information.
<http://www.pfonline.com/>

Websites

<http://www.metal-finishing.com>
<http://www.nmfrc.org>
<http://www.finishing.com>
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